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To advance the fundamental understanding of the electronic bonding, atomic geometry and vibrational properties of ferroelectrics, a first principles linear response approach based on the linearized augmented plane-wave (LAPW) method was developed and applied.



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**Final Report**

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**Contract Period:** 1 Oct 1990 - 30 Sept 1993;
No-cost extension 30 Sept 1993 - 31 Oct 1994

**Performing Organization:** College of William and Mary, P.O. Box 8795, Williamsburg, VA 23187-8795

**Principle Investigator:** Henry Krakauer

**Contract Number:** N00014-91-J-1081

**R & T Project Number:** fmod007---01

**ONR Scientific Officer:** Wallace A. Smith

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January 30, 1995

Dr. Wallace A. Smith
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Dear Dr. Smith:

Please find enclosed three copies of the Final Technical Report on my previous grant N00014-91-J-1081.

Sincerely,

Henry Krakauer
Professor of Physics

cc:

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## A. Description and Motivation of the Scientific Research Goals

To advance the fundamental understanding of the electronic bonding, atomic geometry, and vibrational properties of ferroelectrics, we undertook to develop a first principles linear response approach based on the linearized augmented plane-wave (LAPW) method. The following goals during this grant period were all reached. The motivation for these goals and a more detailed description follows.

1) Develop a first principles LAPW linear response method within the framework of density functional theory.

2) Implement the method into a computer code that is accurate, efficient, and conveniently interfaces with our existing LAPW bandstructure computer code.

3) Benchmark the method on well-studied systems to establish the accuracy of the method.

4) Apply the method to new systems.

Why use linear response theory?

All previous first principles density functional studies of ferroelectrics by our group and by others were based on conventional supercell treatments. These could examine only limited aspects of the phonon spectrum and the structural and vibrational instabilities related to ferroelectric phase transitions. In particular they were limited to studying coherent and periodic structural rearrangements that could be modelled by small supercells. There had been no detailed examinations of the structural instabilities for general wavevectors, although this may be needed to describe the character of the ferroelectric phase transition. The LAPW linear response method that we have developed during this grant period is very powerful, because it permits calculations

of the electronic response to periodic perturbations of arbitrary wavelength, while keeping the computational burden similar to that of a self-consistent calculation for the unperturbed system. Thus, for example, phonon frequencies may be efficiently mapped at all wavevectors throughout the Brillouin zone. Typically in supercell calculations, only selected phonons at the zone center (infinite wavelength) and a few zone boundary phonons could be examined. In addition, Born effective charges and the high-frequency dielectric constants, $\epsilon_\infty$, which are difficult to obtain by other methods are also easily obtained.

Why base the linear response approach on the LAPW method?

The density functional linear response method is relatively new, and most applications have used the pseudopotential method with a plane-wave basis. Ferroelectric materials are very challenging to a plane-wave basis, however, because of the presence of atomic species such as transition metal atoms (e.g., niobium and titanium) and first row atoms (e.g., oxygen), which have localized bonding orbitals. Numerical convergence with the size of the plane-wave basis is a difficulty for these materials. The primary goal of this grant was to implement the linear response theory using a more practical set of basis functions without sacrificing any accuracy. The LAPW method,[1] which has been applied with great success to a variety of physically interesting systems, was chosen for this purpose. The LAPW method uses basis functions that are a combination of plane-waves and localized functions, and it has no difficulty treating such localized orbitals.

**B. Significant Results**

Development of the formalism and testing of the computer code

During this grant period, the formalism[2] for implementing the linear response method in the LAPW method was developed. Developing the formalism was a major task, since unlike plane-wave based methods, the LAPW method employs position dependent basis functions. In analogy with the occurrence of Pulay-type corrections in the calculation of forces using the conventional LAPW method,[3] this positional dependence introduces additional quantities that must be calculated in the LAPW linear response method,[2] significantly modifying the plane-wave based linear response formalism.[4,5] Once the details of this new formalism were worked out on paper, a computer code was developed. It has been thoroughly tested by computing phonon modes for wave vectors $\boldsymbol{q}$ throughout the Brillouin zone in Si and GaAs.[2] Detailed comparisons with conventional LAPW supercell calculations and with experimental vibrational frequencies confirm that accurate results are obtained and that the method can now be used with confidence. Effective charges and the high-frequency dielectric constants, $\epsilon_\infty$, which are difficult to obtain by any other method, were also calculated to be in excellent agreement with previous calculations and experiment for these materials.[2]

Application to the search for multi-well Born Oppenheimer potentials in CuCl

CuCl is known to exhibit large anharmonic effects and possibly a complicated multi-well Born Oppenheimer surface reminiscent of the instabilities in perovskite ferroelectrics, and this was the principle motivating factor for studying this material. Unlike conventional semiconductors such as Si and GaAs, which can also be treated by the plane-wave based linear response approach,

a complete treatment of CuCl,[6] has not been previously published because the localized *3d*-orbitals of the Cu make this material difficult to treat with plane-wave based methods. We calculated its phonon dispersion and found it to be in excellent agreement with experiment, despite the other observed anomalous properties. There was no indication of multi-well potentials. The calculated Born effective charges were within 10% of experiment and the high frequency dielectric constant $\epsilon_\infty$ was about 30% larger than the experimental value (similar overestimates of $\epsilon_\infty$ by density functional calculations are found in simpler materials too). The overall level of agreement with experiment is comparable to that attained by other density functional calculations in simpler semiconductors. Despite the anomalous properties of CuCl and the presence of large anharmonic interactions, linear response calculations provide accurate harmonic phonon dispersion curves. A similar conclusion was reached in the high-$T_c$ superconductors LaCuO and YBCO where calculated frequencies (using a conventional supercell approach) are generally in good agreement with experiment despite perhaps even greater anharmonicity.[7] This is very encouraging for applying the LAPW linear response method to perovskite ferroelectrics.

**C. Impact of this Work on Future Research**

Since the grant period ended, the LAPW linear response method has subsequently been applied to study the ferroelectric phase transitions in perovskite ferroelectrics. A recently completed project[8] examined $KNbO_3$, one of the most extensively studied systems of the perovskite family of ferroelectric materials. The character of its ferroelectric phase transitions (and those of related systems like $BaTiO_3$) has continued to be a subject of controversy. In recent years, the weight of evidence had shifted from a soft-phonon description to support of order-

disorder models, although recent diffuse x-ray scattering experiments seem to support the soft-phonon picture. Previous density functional total energy calculations found $q = 0$ instabilities providing qualitative support for the order-disorder scenario. We have discovered that the instabilities of $KNbO_3$ (and most likely those of related perovskite ferroelectrics) are considerably more complex than previously suspected. We calculated the lattice dynamics, mapping out the instabilities at *all* wavevectors in the Brillouin zone. The principle results found in the ideal $KNbO_3$ perovskite structure are (i) the system is *stable* against displacements of a single Nb atom, and (ii) unstable TO modes exist for $q$ perpendicular to the <100> directions in the BZ. The extent of these modes in the BZ implies instabilities against formation of chains of Nb atoms (mutually uncorrelated) along <100> crystallographic directions. The existence of such chain instabilities had been suggested based on early x-ray measurements, but this is the first time that first principles calculations have provided evidence for this unusual feature.

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8. R. Yu and H. Krakauer, submitted to *Phys. Rev. Lett.*

**D. List of Publications/Reports/Presentations Under This Grant**

Papers Published in Refereed Journals

1) "Linear Response Calculations Using LAPW and Mixed Basis Methods," H. Krakauer, R. Yu, Q. Zhang, D. Singh, C. Haas, and A. Liu, *Ferroelectrics* **136**, 105 (1992).

2) "*Ab Initio* LAPW Linear Response Method for Ferroelectrics," H. Krakauer, R. Yu, and C.-Z. Wang, *Ferroelectrics* **151**, 39 (1994).

3) "Linear Response Calculations within the Linearized Augmented Plane Wave Method," R. Yu and H. Krakauer, *Phys. Rev. B* **49**, 4467 (1994).

4) "First Principles Linear Response Calculations of Lattice Dynamics for CuCl," C.-Z. Wang, R. Yu, and H. Krakauer, *Phys. Rev. Lett.* **72**, 368 (1994)

Presentations - Invited

1) Second Williamsburg Workshop on First-Principles Calculations for Ferroelectricity, 2-4 February 1992: "Linear Response Calculations Using LAPW and Mixed Basis Methods," H. Krakauer, R. Yu, Q. Zhang, D. Singh, C. Haas, and A. Liu, *Ferroelectrics* **136**, 105 (1992).

2) The Eighth International Meeting on Ferroelectricity (IMF8), 8-13 August 1993, Gaithersburg, Maryland: "*Ab Initio* LAPW Linear Response Method for Ferroelectrics," H. Krakauer, R. Yu, and C.-Z. Wang, *Ferroelectrics* **151**, 39 (1994).

**E. Participants and Status**

Henry Krakauer - PI, Professor of Physics

Rici Yu - Postdoctoral Researcher - started on this grant September 1991.

Christopher Lasota Graduate Student [supported by a DOD "Augmentation Award for Science and Engineering Research Training (AASERT)" N00014-93-1095 to this grant.

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